

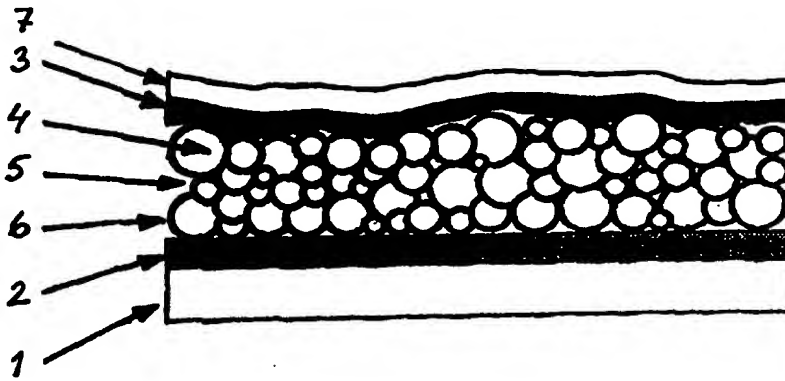
PCT

WORLD INTELLECTUAL PROPERTY
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9608022A1

<p>(51) International Patent Classification ⁶ : H01G 9/20</p>	<p>A1</p>	<p>(11) International Publication Number: WO 96/08022 (43) International Publication Date: 14 March 1996 (14.03.96)</p>
<p>(21) International Application Number: PCT/EP95/03459 (22) International Filing Date: 3 September 1995 (03.09.95) (30) Priority Data: 9402940-2 2 September 1994 (02.09.94) SE (71) Applicant (for all designated States except US): KIETA HOLDING S.A. [CH/CH]; c/o Fiduciaire Transjurane S.A., 8, rue Neuve, CH-2800 Delémont (CH). (72) Inventors; and (75) Inventors/Applicants (for US only): MEYER, Andreas, Felix [CH/CH]; Chemin de la Bossenaz, CH-1173 Fechy (CH). MEYER, Tobias, Balthasar [CH/CH]; Chemin de la Bossenaz, CH-1173 Fechy (CH). (74) Agent: JOHANSSON, Lars; Patech S.A., Le Haut-des-Champs, CH-1173 Fechy (CH).</p>		<p>(81) Designated States: AU, BR, CA, CN, CZ, HU, JP, KR, LK, NZ, PL, RU, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: ELECTROCHEMICAL PHOTOVOLTAIC CELL</p> <p>(57) Abstract</p> <p>In order to provide a more efficient electrochemical photovoltaic cell in which the electrolyte filled gap between the working electrode plate has been eliminated, the counter electrode plate is replaced by a first layer of electrocatalyst material deposited directly on top of the porous metal oxide semiconductor layer on the working electrode. Optionally a second layer of an electrically conductive material, acting as a current collector, can be deposited on top of the first layer comprising the electrocatalyst material.</p> 		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

TITLE

Electrochemical photovoltaic cell

5

TECHNICAL FIELD

The present invention relates to photovoltaic cells, based on the principle of regenerative photoelectrochemical processes.

10

BACKGROUND ART

This type of photovoltaic cells are known from e.g. the International patent application WO 91/16719. This document shows a regenerative photoelectrochemical cell including a first electrode comprising a glass plate, as substrate, coated with an electrically conductive and possibly optically transparent layer on which a thin layer of a metal oxide semiconductor, such as high surface area Titanium dioxide, is deposited. The layer of metal oxide is provided with a monomolecular layer of a sensitizing dye which absorbs the light in the visible part of the spectrum. The dyestuff is cooperating with the oxide by injecting electrons into the conduction band of the same.

A second electrode, the so called "counter electrode", includes a glassplate coated with an electrically conductive and possibly optically transparent layer which in addition might be coated with an electroactive catalyst. The above mentioned electrodes are facing each other and the gap in between is filled with an electrolyte containing a redox couple. The effect of the catalyst is to facilitate the transfer of electrons from the counter electrode to the electrolyte.

In the structure according to the above at least one of the conductive layers has to be transparent so that light can reach the inner part of the cell.

5

Let us assume that light is entering the cell through the counter electrode. The light will then be absorbed by the dye, as described above, and the dye transfers electrons into the conductive band of the semiconductor oxide. The "hole" created in the dye will be "filled" by an electron donated from the electrolyte in the redox process. In an external circuit a load is connected which allows the generated current to circulate. This working principle is previously known from e.g. the document mentioned above.

15

One disadvantage of such a two-plate arrangement where the counter electrode is separated from the working electrode by a gap filled with electrolyte is that large scale manufacturing is made complicated especially when it comes to the arrangement of the internal electrical connections.

20

Furthermore, the gap filled with electrolyte represents an electrical resistance due to the ionic path length, so that the impedance of the cell will be relatively high.

25

Due to the fact that float glass sheets, which are commonly used in the cells, are presenting irregular thicknesses and wavelike deformation on the surface it will be quite difficult to achieve a regular and narrow gap between the two plates, especially for large cells.

30

A further difficulty resides in the fact that when the working electrode plate has been coated with a layer of a highly porous metal oxide semiconductor, it will present an irregular surface. The gap between the top surface of the

35

metal oxide semiconductor layer and the counter electrode plate will also for this reason be irregular.

5 A BRIEF DESCRIPTION OF THE INVENTION

One object of the invention is to provide an electrochemical photovoltaic cell in which the electrolyte filled gap between the working electrode plate and the counter electrode plate
10 has been eliminated. This will give a more efficient cell due to lower internal impedance.

Another object of the invention is to completely eliminate the counter electrode in the form of a second plate which
15 obviously will make the cell much easier to manufacture. There will e.g. be no alignment problems for the glass plates, a cell of the same surface will be less heavy etc..

The above mentioned objects will be achieved in a
20 photovoltaic cell according to the invention by replacing the counter electrode plate by a first layer of electrocatalyst material deposited directly on top of the porous metal oxide semiconductor layer on the working electrode. Optionally a
25 second layer of an electrically conductive material, acting as a current collector, can be deposited on top of the first layer comprising the electrocatalyst material.

With this arrangement of the cell according to the invention the deposited layer of electrocatalyst material will be in
30 intimate contact with the top surface of the porous metal oxide semiconductor layer which thus eliminates the gap filled with electrolyte between the working electrode plate and the counter electrode. The electrolyte necessary for the process is now only present as an impregnation of the
35 semiconductor material. The ionic path will thus be minimized

and will now only be given by the thickness of the porous metal oxide semiconductor layer.

Another advantage of the invention is that it allows a simple
5 manufacturing of photovoltaic cells on curved substrates in
the form of e.g. curved glass plates, with no restrictions on
the curvature. There is as a matter of fact no matching
required anymore between the working electrode plate, usually
made of glass, supporting the metal oxide semiconductor, and
10 the counter electrode, since the electrocatalyst is
intimately following the surface of the porous metal oxide
semiconductor layer, which in its turn follows the shape of
the supporting glass.

15 A additional object of the invention is to provide a method
allowing to manufacture photoelectrochemical cells on
irregular surfaces such as non planar surfaces.

20 BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows schematically a photoelectrochemical cell
according to the prior art.

25 Figure 2 shows the photoelectrochemical cell according to the
invention.

DETAILED DESCRIPTION OF THE INVENTION

30

In order to more clearly show and emphasize the differences
between the prior art and the photoelectrochemical cell
according to the invention an example of a prior art cell is
shown in figure 1.

35

The regenerative photoelectrochemical cell includes a first electrode comprising a glass plate 1, as substrate, coated with an electrically conductive and possibly optically transparent layer 2 on which a thin layer 6 of a metal oxide semiconductor, such as high surface area Titanium dioxide, is deposited. It should be noted that the dimensions and relations between the different dimensions in the figures are not necessarily correct but are chosen to raise the clarity of the figures.

10

The layer of metal oxide 6 is provided with a monomolecular layer of a sensitizing dye which absorbs the light in the visible part of the spectrum. This technique is known from the prior art. The dyestuff is cooperating with the oxide by injecting electrons into the conduction band of the same.

15

A second electrode, the so called "counter electrode", includes a glassplate 8 coated with an electrically conductive and possibly optically transparent layer 7 which in addition might be coated with an electroactive catalyst 3. The above mentioned electrodes are facing each other and the gap in between is filled with an electrolyte 4 containing a redox couple. The effect of the catalyst 3 is to facilitate the transfer of electrons from the counter electrode to the electrolyte 4.

25

In the structure according to the above at least one of the conductive layers 2, 7 has to be transparent so that light can reach the inner part of the cell.

30

The functioning of a cell according to the prior art has been described above.

As mentioned above it would be possible using the inventive principle to utilize e.g. a curved glass tile as the

35

substrate on which the whole photoelectrochemical cell is build up layer by layer. For the sake of simplicity, however, the cell according to the invention, figure 2, has been shown as a flat structure

5

The working electrode of the cell according to the invention has a similar structure as the corresponding electrode in the cell according to the prior art. The same designations have been used for corresponding parts.

10

The counter electrode in the cell according to the invention consists of a layer 3 of an electrocatalyst and preferably a current collecting layer 7. These layers are directly deposited on top of the semiconductor layer 6 which itself is deposited on a plate 1 coated with an electrically conductive and optically transparent layer 2. As in the cell according to the prior art the semiconductor layer is preferably impregnated with sensitizing dye 5.

20 The electrolyte 4 is filling the interstices between the metal oxide semiconductor crystallites, and is thus retained by capillarity.

The plate 1 could be of glass or another suitable material.

25 Due to the process for depositing the semiconductor layer the material should be heat resistant.

The electrically conductive layer 2 could e.g. comprise fluorine doped tin oxide or indium oxide doped with tin oxide.

30 And the semiconductor layer could comprise titanium oxide or another wide-band semiconductor material typically a metal oxide deposited with methods according to prior art.

CLAIMS

- 5
1. Regenerative electrochemical photovoltaic cell comprising a first and a second electrode, the first electrode including a plate (1) as substrate, coated with an electrically conductive layer (2), a layer (6) of a semiconductor material applied on said layer (2), an electrolyte (4) impregnating said layer (6) characterised in that an electroactive catalyst (3) is deposited directly on the top surface of said semiconductor layer (6) which catalyst layer will act as said second electrode.
- 10
- 15
- 2- Photovoltaic cell according to claim 1 characterised in that the plate (1) is a glass plate.
- 20
3. Photovoltaic cell according to claim 1 or 2 characterised in that the layer (2) is optically transparent.
- 25
4. Photovoltaic cell according to any of the claims 1 to 3 characterised in that the layer (6) is a porous, high surface area metal oxide semiconductor.
- 30
5. Photovoltaic cell according to claim 4 characterised in that the metal oxide semiconductor comprises titanium dioxide.
- 35
6. Photovoltaic cell according to any of the claims 1 to 5 characterised in that an electrically conductive layer (7) is

deposited on top of said electroactive catalyst (3) and constitutes a current collector.

- 5 7. Photovoltaic cell according to claim 6 characterised in that the electrically conductive layer (7) is optically transparent.

1/1

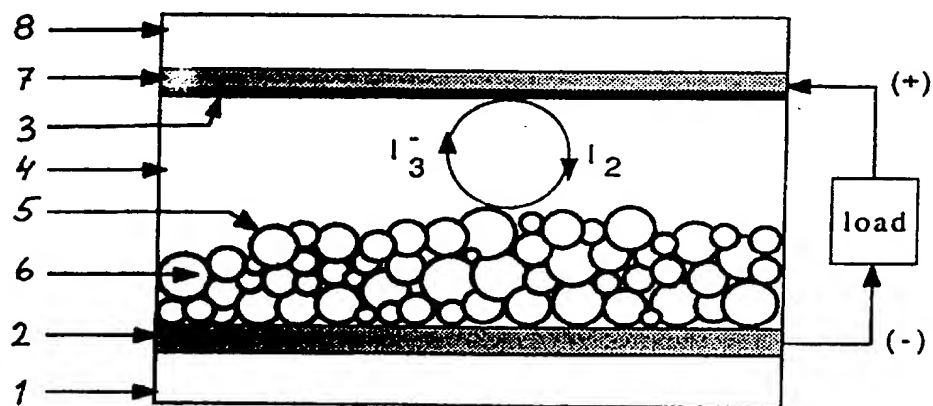


FIG. 1

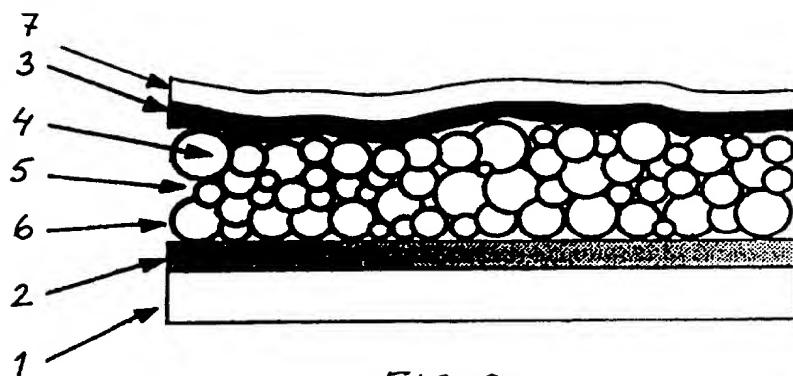


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 95/03459

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01G9/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,91 16719 (GRAETZEL, MICHAEL) 31 October 1991 cited in the application -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

Date of the actual completion of the international search

18 December 1995

Date of mailing of the international search report

05.01.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Goossens, A

INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/EP 95/03459

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9116719	31-10-91	AU-B- 650878	07-07-94
		AU-B- 7748391	11-11-91
		EP-A- 0525070	03-02-93
		JP-T- 5504023	24-06-93
		US-A- 5350644	27-09-94
